



Spectroscopic Investigations on Nanostructured ZnS Films

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Nanostructured zinc sulphide (ZnS) films have been synthesized on glass substrates by chemical bath deposition (CBD) method at room temperature. X-ray diffraction (XRD) study exhibits formation of nanocrystals having cubic zinc blended structure of ZnS and crystallite size of the prepared sample has been estimated. Study on the properties of chemical composition is investigated by Fourier Transform Infra Red (FTIR) Spectroscopy. Optical study is carried out with the help of photoluminescence (PL) spectroscopy.

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Nanostructured ZnS films, XRD, FTIR, PL

INTRODUCTION

BSTRA

In recent years nanostructured materials have attracted much attention due to their novel properties. Semiconductor nanocrystals of II-VI group have gained much interest among researchers and manufacturers due to their unique properties and potential applications in numerous fields. ZnS belongs to II-VI group with direct band gap of 3.68 eV at room temperature and high refractive index (2.35 at 632 nm). Nanostructured ZnS films have unique physical, optical, electrical, chemical and transport properties, which are quite different from its bulk counterpart. It is a nontoxic as well as possesses good thermal stability and has potential applications in numerous areas such as in optical filters, sensors¹, solar cells², IR window, laser, optoelectronics devices, field-effect transistors, ultraviolet light emitting diodes³⁻⁴, optical switches, photocatalysis, photocells, etc. It also finds applications in pharmaceutical product, water purification, paints and many more. Different workers have adopted various techniques to synthesis nanostructured ZnS film. Some of them are Chemical bath deposition (CBD)⁵, chemical vapour deposition, molecular beam epitaxy⁶, reverse micelle method⁷, sol-gel method⁸, sputtering method⁹, electro deposition¹⁰ and chemical method¹¹, etc. In our work we have adopted Chemical bath deposition (CBD) method to synthesis nanostructued ZnS films because the method is simple and cost effective.

EXPERIMENTAL DETAILS

Nanostructured ZnS films were prepared in the polyvinyl alcohol (PVA) matrix using ZnCl₂ and Na₂S as the source materials of Zn²⁺ and S²⁻ ions respectively. PVA was used as the capping agent. The matrix solution was prepared by adding Zinc Chloride solution (having 0.5 molarity) to an aqueous solution (4wt %) of polyvinyl alcohol (PVA) under a high stirring rate (200rpm) condition. During the process of stirring a constant temperature 70°C was maintained for 3 hours and the sample under preparation was kept for 12 hours. Next, Na₂S solution having 0.25 molarity was added to the above solution till the whole solution appears milky. The final solution was casted onto the cleaned glass substrates and is allowed to dry in a closed chamber at room temperature to produce nanostructued ZnS films.

RESULTS AND DISCUSSION The X-ray diffraction (XRD) study

XRD patterns of the prepared ZnS films were recorded by PANalytical X'Pert Pro X-ray diffractometer. Fig.1 exhibits the XRD pattern of the prepared sample which shows three clear and prominent diffraction peaks centered at 2θ =28.95, 48.315 and 57.12. These diffraction peaks correspond to (111), (220) and (311) planes respectively and they are indexed as cubic zinc blended structure of ZnS (JCPDS: 800020). The diffraction peak position of (111) plane shifts slightly by an amount 0.04 towards higher diffraction angle (20) from its corresponding value for bulk ZnS (2 θ =28.91; JCPDS 800020) which indicates generation of compressive stress. The broadening and intense of diffraction peak

profile suggests formation of nanocrystals and good cryastalline nature of sample.



Fig. 1 XRD pattern of nanostructured Zn film

The average crystallite size of the ZnS film is calculated using Scherrer's formula $^{\rm ^{12}}$

(1)

$$D = \frac{K\lambda}{\beta_{\rm D}\cos\theta}$$

where K is a constant taken equal to 0.94, λ is the wavelength of the radiation which is 1.54056 Å for CuK α radiation, β_0 (in radian) is the full width at half maximum (FWHM) of the peaks and θ is the Bragg's diffraction angle. The estimated average crystallite size is found to be 5.26 nm.

Fourier transform infra red (FTIR) study

The FTIR spectroscopy is a useful technique to find the functional group. It can be used to measure the bond vibration frequency in a molecule. Fourier transform infra red (FTIR) spectra of nanostructured ZnS films were recorded in IR Affinity-1, SHIMADZU in the wavelength range of 4000 to 450 cm⁴. Fig. 2 shows FTIR spectra of ZnS sample prepared in PVA matrix at room temperature.



Fig. 2 FTIR spectra of nanostructured ZnS film

The absorption band centered at 3367 cm⁻¹ is attributed to the O–H stretching vibration of water molecule¹³. The band at 2364 cm⁻¹ is due to C-H stretching. C=O stretching appears at 1624 cm⁻¹. The absorption band which appears at 1420 cm⁻¹ is assigned to C-H stretching. Trace amount of SO₄⁻ is observed with

the appearance of absorption band at 1114 cm⁻¹¹⁴.

Photoluminescence study

Photoluminescence emission spectra of nanostructured ZnS film deposited on glass substrate was recorded in F-2500 Fluorescence spectrophotometer and it is shown in Fig. 3.



Fig. 3 PL emission spectra of nanostructured ZnS film

Photoluminescence emission spectrum contains two peaks centered at 422 nm and 462 nm. The appearance of peak at 422 nm is attributed to Sulphur vacancies in the lattice¹⁵⁻¹⁶. The blue emission centered at 462 nm is because of the recombination between conduction band and zinc vacancy related acceptor¹⁷.

CONCLUSION

Good quality of nanostructured ZnS films have been prepared by CBD method. XRD study shows the formation of cubic zinc blended structure of ZnS. Study of FTIR spectra exhibits the stretching modes of the sample. From The PL study emission centers are observed and it is fond to consist of two peaks at 422 nm and 462 nm.

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